Precision spectroscopy of the hydrogen molecular ion HD^+

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Expectation values of the Breit operators and the Q terms are calculated for HD^+ with the vibrational number $v = 0-4$ and the total angular momentum $L = 0-4$. Relativistic and radiative corrections to some ro-vibrational transition frequencies are determined. Numerical uncertainty in $R_\infty\alpha^2$ order correction is reduced to sub kHz or smaller. Our work provides an independent verification of Korobov's calculations [Phys. Rev. A **74**, 052506 (2006); **77**, 022509 (2008)].

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I. INTRODUCTION

Hydrogen molecular ions, such as H_2^+ and HD^+, can be used [1, 2] to deduce an improved value of the proton-electron mass ratio by comparing experimental and theoretical spectroscopic data. To this end, several experiments have been setup for measuring high precision transition frequencies in HD^+ [3, 4] and H_2^+ [5]. For HD^+ in particular, the $(v, L) = (4, 3) \to (0, 2)$ transition frequency has been measured at the 2 ppb level [3]. In order to reduce the current uncertainty of 4.1×10^{-10} [6] in the proton-electron mass ratio, both experiment and theory should reach a precision of sub-kHz or better.

For light systems, nonrelativistic QED (NRQED) [7, 8] approach is used to expand the energy in powers of the fine structure constant α. Nonrelativistic energies of H_2^+ and HD^+ have been variationally calculated at the precision of 10^{-15} [2, 9] for a wide range of vibrational states and at the precision of 10^{-30} [10–14] for some low vibrational states. Relativistic and radiative corrections of order $R_\infty\alpha^2$, $R_\infty\alpha^3$, $R_\infty\alpha^4$, and $R_\infty\alpha^5$ have been systematically calculated [15, 16] for H_2^+ and HD^+ ro-vibrational states ($v = 0-4, L = 0-4$). The leading order $R_\infty\alpha^2$ relativistic corrections are now available with very high precision for the H_2^+ vibrational states $(0, 0)$, $(1, 0)$, and $(0, 1)$ [17]. Recently, improved values of $R_\infty\alpha^3$ order corrections have been achieved by an intensive calculation of the Bethe logarithm term [18].

The purpose of this Brief Report is to present our independent calculations of the Breit operators and the Q terms for the HD^+ ro-vibrational states ($v = 0-4, L = 0-4$). Some important ro-vibrational transition frequencies are determined, which provides a verification of Korobov's theoretical work. In addition, the numerical results presented here might serve as a benchmark for other theoretical methods. We use atomic units ($\hbar = e = m_e = 1$), unless otherwise stated. The fundamental physical constants involved are taken from the 2010 CODATA recommended values [6].

II. THEORY

Consider the hydrogen molecular ion HD^+. After separating the center of mass coordinates for the system, the eigenvalue problem for the nonrelativistic Hamiltonian H_0 becomes [14]

$$H_0\Psi = E_0\Psi\,, \tag{1}$$

$$H_0 = \lambda_1\nabla_{r_1}^2 + \lambda_2\nabla_{r_2}^2 + \lambda_{12}\nabla_{r_1}\cdot\nabla_{r_2} + V\,, \tag{2}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ represent respectively the position vectors of the electron and proton, relative to the deuteron situated at the origin, $\lambda_1 = -(1 + m_d)/(2m_d)$, $\lambda_2 = -(1/m_d + 1/m_p)/2$, $\lambda_{12} = -1/m_d$, $V = -1/r_1 + 1/r_2 - 1/r_{12}$ is the Coulomb interaction, and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. The energy eigenvalue problem for H_0 is solved variationally using the basis set in Hylleraas coordinates

$$\phi_{ijk}(\mathbf{r}_1, \mathbf{r}_2) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2}\mathcal{Y}_{l_1 l_2}^{LM}(\mathbf{r}_1, \mathbf{r}_2)\,, \tag{3}$$

where $\mathcal{Y}_{l_1 l_2}^{LM}(\mathbf{r}_1, \mathbf{r}_2)$ is the vector coupled product of spherical harmonics for the electron and the proton to form a common eigenvector of L^2 and L_z. More details on the construction of basis set for HD^+ may be found in [12, 14]. It should be pointed out that this basis set differs from the one used by Korobov [15, 16]. The basic type of integrals required in the calculation of matrix elements can be evaluated analytically [19] using Perkins' expansion for r_{12}^k. The procedure for handling singular integrals that appear in the evaluation of Breit operators can be found in [20].

The leading-order relativistic corrections due to the Breit operators are well established, which can be found in Refs. [21–23]. The complete spin-independent part of order $R_\infty\alpha^2$ term is

$$E^{(2)} = \alpha^2\langle H_{\rm Breit}\rangle\,, \tag{4}$$

where

$$\begin{aligned} H_{\rm Breit} &= -\frac{1}{8}\nabla_{r_1}^4 - \frac{1}{8m_p^3}\nabla_{r_2}^4 - \frac{1}{8m_d^3}(\nabla_{r_1} + \nabla_{r_2})^4 \\ &+ \frac{\pi}{2m_p^2}\delta(\mathbf{r}_{12}) + \frac{\pi}{2}\left[\delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12})\right] \\ &- R_{de} + R_{dp} - R_{pe}\,, \end{aligned} \tag{5}$$

where

$$R_{de} = \frac{-1}{2m_d}\left(\frac{\nabla_{r_1}\cdot(\nabla_{r_1}+\nabla_{r_2})}{r_1}+\frac{\mathbf{r}_1\mathbf{r}_1:(\nabla_{r_1}+\nabla_{r_2})\nabla_{r_1}}{r_1^3}\right)$$
$$R_{dp} = \frac{-1}{2m_dm_p}\left(\frac{\nabla_{r_2}\cdot(\nabla_{r_1}+\nabla_{r_2})}{r_2}+\frac{\mathbf{r}_2\mathbf{r}_2:(\nabla_{r_1}+\nabla_{r_2})\nabla_{r_2}}{r_2^3}\right)$$
$$R_{pe} = \frac{1}{2m_p}\left(\frac{\nabla_{r_1}\cdot\nabla_{r_2}}{r_{12}}+\frac{\mathbf{r}_{12}\mathbf{r}_{12}:\nabla_{r_1}\nabla_{r_2}}{r_{12}^3}\right).$$

In the above, the Darwin term $\pi/(2m_p^2)\delta(\mathbf{r}_{12})$ is the nuclear spin dependent recoil correction for the spin-$\frac{1}{2}$ particle, such as proton. This term vanishes in case of spin-0 or spin-1 nucleus, such as the ^{4}He nucleus or deuteron [24]. It is noted that $\delta(\mathbf{r}_2)$ is virtually zero due to the molecular nature of the system.

Furthermore, the spin-independent radiative correction of order $R_\infty\alpha^3$ may be expressed as [25–27]:

$$E^{(3)} = \alpha^3\left\{\frac{4}{3}\left[-\ln\alpha^2-\beta(v,L)+\frac{19}{30}\right]\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_{12})\rangle + \frac{2}{3}\left[-\ln\alpha-4\beta(v,L)+\frac{31}{3}\right]\left[\frac{\langle\delta(\mathbf{r}_1)\rangle}{m_d}+\frac{\langle\delta(\mathbf{r}_{12})\rangle}{m_p}\right] - \frac{14}{3}\left[\frac{Q(\mathbf{r}_1)}{m_d}+\frac{Q(\mathbf{r}_{12})}{m_p}\right]\right\}, \quad (6)$$

where $\beta(v,L)$ is the Bethe logarithm, $Q(\mathbf{r}_1)$ and $Q(\mathbf{r}_{12})$ are the Q terms introduced by Araki and Sucher [28],

$$Q(\mathbf{r}) = \lim_{\rho\to0}\left\langle\frac{\Theta(r-\rho)}{4\pi r^3}+(\ln\rho+\gamma_E)\delta(\mathbf{r})\right\rangle, \quad (7)$$

and γ_E is the Euler gamma constant.

For higher order corrections, such as orders $R_\infty\alpha^4$ and $R_\infty\alpha^5$, we follow the work of Ref. [16]. Thus, $R_\infty\alpha^4$ order non-recoil relativistic and radiative corrections may be express as follows [16]:

$$E^{(4)} = \alpha^4\left\{\frac{1}{\pi}\left[-\frac{2179}{648}+\frac{3523}{864}\pi^2-\frac{1}{2}\pi^2\ln2-\frac{9}{4}\zeta(3)\right]\times\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_{12})\rangle+E^{(4)}_{\rm rel}\right\}, \quad (8)$$

where $E^{(4)}_{\rm rel}$ is the $R_\infty\alpha^4$ order relativistic correction.

Since the electron is almost bounded in the ground state of hydrogen molecular ion, its wave function can be approximately expressed as a linear combination of two hydrogen-like wave functions $\psi_e(\mathbf{r}_e) = C[\psi_{1s}(\mathbf{r}_1)+\psi_{1s}(\mathbf{r}_{12})]$. Therefore, the most important $R_\infty\alpha^5$ order correction can be estimated using this approximate wave function [16, 23]

$$E^{(5)} = \alpha^5\left[-\ln^2\frac{1}{(\alpha)^2}+A_{61}\ln\frac{1}{(\alpha)^2}+A_{60}+\frac{B_{50}}{\pi}\right]\times\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_{12})\rangle, \quad (9)$$

where the constants A_{61}, A_{60}, and B_{50} are taken to be the constants of the $1s$ state of the atomic hydrogen, *i.e.*, $A_{61} = 5.419\cdots$ [29], $A_{60} = -30.924\cdots$ [30], and $B_{50} = -21.556\cdots$ [31].

TABLE I: Convergence study of the expectation values of $\delta(\mathbf{r}_1)$ and $\delta(\mathbf{r}_{12})$ for the HD^+ $(v=4, L=4)$ state, where N is number of basis functions.

N	$\delta(\mathbf{r}_1)$	$\delta(\mathbf{r}_{12})$
2789	0.188 729 941 487	0.188 382 948 5531
3415	0.188 729 516 647	0.188 382 898 6629
4130	0.188 729 943 378	0.188 382 886 4800
4940	0.188 729 938 954	0.188 382 884 0699
5851	0.188 729 935 696	0.188 382 876 7837
6859	0.188 729 935 329	0.188 382 876 7442
8000	0.188 729 935 332	0.188 382 876 7368
9250	0.188 729 935 329	0.188 382 876 7376
Extrp.	0.188 729 935 323(7)	0.188 382 876 7375(1)

In addition to the relativistic and radiative corrections, one also needs to consider the contribution from the finite nuclear charge distribution. The leading-order correction is

$$E_{\rm nuc} = \frac{2\pi}{3}\left[\left(\frac{R_d}{a_0}\right)^2\langle\delta(\mathbf{r}_1)\rangle+\left(\frac{R_p}{a_0}\right)^2\langle\delta(\mathbf{r}_{12})\rangle\right], \quad (10)$$

where $R_p = 0.8775(51)$ fm and $R_d = 2.1424(21)$ fm [6] are the root-mean-square charge radii of proton and deuteron respectively.

III. RESULTS

With the Hylleraas-type basis set of Eq. (3), the wave functions along with the corresponding nonrelativistic energies are obtained by solving Eq. (1) variationally. Then the expectation values of the Breit operators can be evaluated. In particular, the global operator method [32] is applied to the evaluations of $\nabla^4_{r_1}$, $\nabla^4_{r_2}$, $(\nabla_{r_1}+\nabla_{r_2})^4$, $\delta(\mathbf{r}_1)$, and $\delta(\mathbf{r}_{12})$. As an example, Table I shows a convergence study for the expectation values of $\delta(\mathbf{r}_1)$ and $\delta(\mathbf{r}_{12})$. One can see that an accuracy of about 11-12 significant figures is achieved for the most difficult state of $(4,4)$, where the nonrelativistic energy is calculated only to 16 digits. For ro-vibrational states ($v=0$–$4, L=0$–4), numerical results of the Breit operators are presented in Tables II and III, together with a comparison with Korobov's values [15]. Results for the Q terms are listed in Tables V and IV. All expectation values are in good agreement with Korobov's values, although our results are more precise. The largest size of basis set used here is about 9000.

We summarize the contributions up to $R_\infty\alpha^5$ to two ro-vibrational transition frequencies in Table VI, where the values of the Bethe logarithm are taken from Ref. [18] and the $R_\infty\alpha^4$ order relativistic correction $E^{(4)}_{\rm rel}$ taken from Ref. [16]. For the $(1,0)\to(0,0)$ transition, the numerical uncertainty in ΔE_{α^2} has been reduced from 1 kHz in Korobov's value to the present 8 Hz, which is due entirely to the uncertainties in the fundamental constants.

TABLE II: Expectation values of $\delta(\mathbf{r}_1)$, $\delta(\mathbf{r}_{12})$, $\nabla^4_{r_1}$, $\nabla^4_{r_2}$, and $(\nabla_{r_1}+\nabla_{r_2})^4$ for HD^+ with $v=0-4$ and $L=0-4$. Korobov's results [15] are listed in the second entry of each ro-vibrational state.

(v,L)	$\delta(\mathbf{r}_1)$	$\delta(\mathbf{r}_{12})$	$\nabla^4_{r_1}$	$\nabla^4_{r_2}$	$(\nabla_{r_1}+\nabla_{r_2})^4$
$(0,0)$	0.20734814178029706(2)	0.20704259947747190(4)	6.3001999476785933(6)	104.371713686093(1)	104.443848901053(2)
	0.207348142	0.207042599	6.30019995	104.372	104.444
$(1,0)$	0.20260117861162289(2)	0.20228886473978993(2)	6.15902235229201(4)	449.45675946471(2)	449.7391462670(1)
	0.202601179	0.202288865	6.15902236	449.457	449.739
$(2,0)$	0.19816679512560184148)	0.19784583746893604(2)	6.02761432267228(1)	1042.81683129264(3)	1043.44331653088(5)
	0.198166795	0.197845838	6.02761433	1042.82	1043.443
$(3,0)$	0.1940278413804545(3)	0.1936960139249636(3)	5.9054534324885(7)	1812.997565364(1)	1814.063236354(2)
	0.194027841	0.193696014	5.90545344	1813.00	1814.06
$(4,0)$	0.19016909089076(3)	0.189823702852585(7)	5.7920773795339(5)	2697.669274(1)	2699.2354157(9)
	0.190169092	0.189823704	5.79207742	2697.67	2699.24
$(0,1)$	0.207163241677423572(7)	0.20685769957275256(1)	6.294450746055923(5)	110.38493981778(2)	110.4613313632(1)
	0.207163242	0.206857700	6.29445075	110.385	110.461
$(1,1)$	0.20242655716340313(3)	0.20211421220190804(1)	6.15359974575108(2)	464.36193814804(1)	464.6533872074(1)
	0.202426557	0.202114213	6.15359977	464.362	464.653
$(2,1)$	0.198001981206342(1)	0.197680959785677(9)	6.0225036774882(2)	1064.624132727(1)	1065.263406622(4)
	0.198001983	0.197680957	6.02250376	1064.62	1065.26
$(3,1)$	0.193872416785920(1)	0.193540478376632(6)	5.9006418093939(4)	1839.951687858(5)	1841.032921943(3)
	0.193872418	0.193540480	5.90064189	1839.95	1841.03
$(4,1)$	0.1900226872284(1)	0.18967713560504(1)	5.787553428565(6)	2728.2144158(1)	2729.7980517(2)
	0.190022692	0.189677140	5.78755367	2728.21	2729.80
$(0,2)$	0.206795444334944O(4)	0.20648990097608551(7)	6.2830163299151(5)	123.79001412764(6)	123.8756587418(6)
	0.206795445	0.206489902	6.28301636	123.790	123.876
$(1,2)$	0.2020792303568918(5)	0.2017668215015289(1)	6.142815739370(1)	495.3679016186(8)	495.678116390(6)
	0.202079231	0.201766822	6.14281577	495.368	495.678
$(2,2)$	0.197674187318997O(5)	0.19735302511804O(5)	6.012340962862(5)	1109.271531087(7)	1109.93693530(3)
	0.197674189	0.197353027	6.01234104	1109.27	1109.94
$(3,2)$	0.193563323743184(3)	0.193231161405204(1)	5.89107464757(3)	1894.7472155(5)	1895.8600500(8)
	0.193563325	0.193231163	5.89107470	1894.75	1895.86
$(4,2)$	0.189731562326548)	0.189385681215803)	5.77855925079(2)	2790.0612310(3)	2791.6802590(4)
	0.189731566	0.189385688	5.77855952	2790.06	2791.68
$(0,3)$	0.206248697O164612(4)	0.20594314768281(1)	6.266022789768(7)	147.25876381(2)	147.36009295(4)
	0.206248697	0.205943148	6.26602281	147.259	147.360
$(1,3)$	0.2015629737358(2)	0.2012504647824(3)	6.1267909226(3)	544.7845009(2)	545.1244240(5)
	0.201562974	0.201250465	6.12679095	544.785	545.124
$(2,3)$	0.19718702654295(2)	0.19686565432911(8)	5.9972415652(1)	1178.74702791(2)	1179.4529688(1)
	0.197187028	0.196865656	5.99724165	1178.75	1179.45
$(3,3)$	0.19310402152252(7)	0.192771518257(4)	5.876862410(2)	1979.084658(2)	1980.246050(8)
	0.193104023	0.192771520	5.87686248	1979.08	1980.25
$(4,3)$	0.18929902980(2)	0.18895264869(6)	5.7652006889(6)	2884.65201(1)	2886.32533(6)
	0.189299034	0.188952656	5.76520094	2884.65	2886.33
$(0,4)$	0.205528777980949(6)	0.20522321312906(3)	6.24365466610(2)	184.59247475(2)	184.7179604(1)
	0.205528778	0.205223214	6.24365467	184.592	184.718
$(1,4)$	0.20088331251301(2)	0.2005706622275(5)	6.1057017310(3)	615.8801839(4)	616.262509(1)
	0.200883313	0.200570663	6.10570175	615.880	616.262
$(2,4)$	0.1965457848848(2)	0.1962241242204(1)	5.97737426240(4)	1275.84569327(1)	1276.6080713(2)
	0.196545786	0.196224126	5.97737434	1275.85	1276.61
$(3,4)$	0.192499569868(1)	0.192166602681(1)	5.8581666305(8)	2095.33663918(2)	2096.564775(2)
	0.192499571	0.192166604	5.85816669	2095.34	2096.56
$(4,4)$	0.188729935323(7)	0.1883828767375(1)	5.747632304(5)	3013.980528(6)	3015.72739(3)
	0.188729937	0.188382879	5.74763241	3013.98	3015.73

The correction ΔE_{α^3} to this transition has been obtained in Ref. [18] and reproduced here. The recoil correction of $R_\infty\alpha^4(m/M)$ and higher contributes at the level of relative $10^{-10}-10^{-11}$, which causes a theoretical uncertainty of 1 kHz in ΔE_{α^4}. The largest uncertainty for the transition $(1,0)\to(0,0)$ comes from the theoretical uncertainty of ΔE_{α^5}. The uncertainty in $\Delta E_{\rm nuc}$ is due to the uncertainties in the proton and deuteron charge radii. For the transition $(4,3)\to(0,2)$, both experimental [3] and theoretical [16] results are available. In our calculation for this transition, although the uncertainties in ΔE_{α^2} and ΔE_{α^3} have been reduced to sub kHz, the

TABLE III: Expectation values of R_{dp}, R_{de}, and R_{pe} for HD^+ with $v = 0-4$ and $L = 0-4$. Korobov's results [15] are listed in the second entry of each ro-vibrational state.

(v, L)	R_{dp}	R_{de}	R_{pe}
$(0, 0)$	5.35463051901711943(7)	1.17448782593260556(3)	1.1707701450511397 27(2)
	5.35463	1.17449	1.17077
$(1, 0)$	15.14482588936280077(6)	1.1504812637673131(2)	1.1433664050045(2)
	15.1448	1.15048	1.14337
$(2, 0)$	23.59899696623698(2)	1.128236200892749 4(6)	1.1181235693136(2)
	23.5990	1.12824	1.11812
$(3, 0)$	30.817653008622(1)	1.10767720643593(3)	1.0949375427689(2)
	30.8177	1.10768	1.09494
$(4, 0)$	36.88807887511(1)	1.088739929649(8)	1.073718403917(3)
	36.8881	1.08874	1.07372
$(0, 1)$	5.589562255342723(1)	1.1735785001855910(1)	1.1697193799366195(4)
	5.58956	1.17358	1.16972
$(1, 1)$	15.350575279863064(1)	1.1496258585220391(3)	1.14238073961236855(7)
	15.3506	1.14963	1.14238
$(2, 1)$	23.777762089355404(4)	1.1274325102467439(1)	1.11720015102388(1)
	23.7778	1.12743	1.11720
$(3, 1)$	30.97134959374(1)	1.1069233223353(1)	1.09407389213715(9)
	30.9713	1.10692	1.09407
$(4, 1)$	37.0183653341(6)	1.08803423109(2)	1.07291239499(1)
	37.0184	1.08803	1.07291
$(0, 2)$	6.055104818249343733(4)	1.171769108405540(2)	1.16762928124835329(3)
	6.05510	1.17177	1.16763
$(1, 2)$	15.75802763752410(4)	1.147923888699637(7)	1.140420315240445(2)
	15.7580	1.14792	1.14042
$(2, 2)$	24.13150123361982(4)	1.12583357622946(1)	1.11536372709830(3)
	24.1315	1.12583	1.11536
$(3, 2)$	31.275189712792(3)	1.1054236322514(2)	1.0923565391832(2)
	31.2752	1.10542	1.09236
$(4, 2)$	37.275607599566(2)	1.086630566009(1)	1.07130988884988(7)
	37.2756	1.08663	1.07131
$(0, 3)$	6.74277630617217739(6)	1.16907791520748(2)	1.1645223841766(2)
	6.74278	1.16908	1.16452
$(1, 3)$	16.35924480624(3)	1.145392790044(2)	1.13750662824(1)
	16.3592	1.14539	1.13751
$(2, 3)$	24.6527816700128(9)	1.1234560568468(8)	1.112634817630(2)
	24.6528	1.12346	1.11263
$(3, 3)$	31.72221152212(6)	1.10319406478 0(2)	1.0898050864(1)
	31.7222	1.10319	1.08981
$(4, 3)$	37.65328339(4)	1.0845441798(5)	1.068929626(1)
	37.6533	1.08454	1.06893
$(0, 4)$	7.640242669140628(6)	1.16553169532956(5)	1.1604316913454(5)
	7.64024	1.16553	1.16043
$(1, 4)$	17.1426952788899(3)	1.1420581168039(4)	1.133671151272(3)
	17.1427	1.14206	1.13367
$(2, 4)$	25.3308170266259(7)	1.120324362118(2)	1.109043458742(1)
	25.3308	1.120320	1.10904
$(3, 4)$	32.30232200847(1)	1.100257957806(8)	1.086448221081(5)
	32.3023	1.10026	1.08645
$(4, 4)$	38.14194609(1)	1.0817974074(2)	1.0657990275(3)
	38.1419	1.08180	1.06580

total uncertainty in the transition frequency remains as large as 70 kHz, which is from the ΔE_{α^5} term.

In summary, we have presented an independent calculation of the Breit operators and the Q terms for the HD^+ ro-vibrational states ($v = 0-4, L = 0-4$), which provides a verification of previous theoretical results.

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TABLE IV: Numerical values of $Q(\mathbf{r}_1)$ for HD^+ with $v = 0-4$ and $L = 0-4$, where the second entry lists Korobov's results [15].

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$L=0$	–0.1348622766081903(2)	–0.132113355129(1)	–0.129551987571271(1)	–0.1271692904455(1)	–0.12495749557739(3)
	–0.13486	–0.13211	–0.12955	–0.12717	–0.12496
$L=1$	–0.134742001057392(5)	–0.13199961143967(2)	–0.1294445278685(4)	–0.1270678977803(2)	–0.1248619827842(2)
	–0.13474	–0.13200	–0.12944	–0.12707	–0.12486
$L=2$	–0.13450284686085(8)	–0.1317734666211(3)	–0.1292308990657(3)	–0.126866353373(3)	–0.1246721506275(1)
	–0.13450	–0.13177	–0.12923	–0.12687	–0.12467
$L=3$	–0.1341475653900(1)	–0.131437564457(6)	–0.12891364214(1)	–0.12656709998(4)	–0.124390349(3)
	–0.13415	–0.13144	–0.12891	–0.12657	–0.12439
$L=4$	–0.1336801802328(6)	–0.130995769843(4)	–0.128496470584(6)	–0.12617370653(3)	–0.1240200070(4)
	–0.13368	–0.13100	–0.12850	–0.12617	–0.12402

TABLE V: Numerical values of $Q(\mathbf{r}_{12})$ for HD^+ with $v = 0-4$ and $L = 0-4$, where the second entry lists Korobov's results [15].

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$L=0$	–0.1345911955685105(1)	–0.131838977797(3)	–0.129272929986259(7)	–0.1268839283180(2)	–0.12466388687278(6)
	–0.13459	–0.13184	–0.12927	–0.12688	–0.12466
$L=1$	–0.13447097875759(1)	–0.131725268104580(5)	–0.1291654760689(3)	–0.1267825085601(1)	–0.1245683078029(8)
	–0.13447	–0.13172	–0.12916	–0.12678	–0.12457
$L=2$	–0.13423194023120(3)	–0.1314991894516(1)	–0.1289518569532(7)	–0.126580907975(1)	–0.124378340936(7)
	–0.13423	–0.13150	–0.12895	–0.12658	–0.12438
$L=3$	–0.133876827784(1)	–0.13116338201(2)	–0.12863460989(3)	–0.1262815656(3)	–0.12409633(1)
	–0.13388	–0.13116	–0.12863	–0.12628	–0.12410
$L=4$	–0.13340659744(2)	–0.13072170536(5)	–0.12821744286(1)	–0.1258880438(2)	–0.12372570179(5)
	–0.13341	–0.13072	–0.12822	–0.12589	–0.12373

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TABLE VI: Summery of contributions to the HD^+ transition frequencies (in MHz).

	$(4,3) \to (0,2)$	$(1,0) \to (0,0)$	
Author	Present	Present	Korobov [16]
$\Delta E_{\rm nr}$	214 976 047.328 2(6)	57 349 439.973 34(14)	57 349 439.9717
ΔE_{α^2}	3 411.702 93(4)	958.276 694(8)	958.277(01)[a]
ΔE_{α^3}	–891.610 9(1)	–242.126 26(4)	–242.125(02)
ΔE_{α^4}	–6.457(1)	–1.748(1)	–1.748
ΔE_{α^5}	0.388(74)	0.105(20)	0.105(19)
$\Delta E_{\rm nuc}$	–0.462(6)	–0.125 2(17)	–0.125(2)[a]
$\Delta E_{\rm tot}$	214 978 560.88(7)	57 350 154.355(22)	
$E_{\rm theor}$ [16]	214 978 560.88(7)		57 350 154.355(21)
$E_{\rm expt}$ [3]	214 978 560.6(5)		

[a]Obtained using the data of Table V in Ref. [15].

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